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Co -solvent method produce biodiesel form waste cooking oil with small pilot plant

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Abstract

In this study, we studied the production of biodiesel from waste cooking oil with co-solvent technology. A co-solvent technology with acetone has many advantage, but needs to remove solvents dissolved in the mixture. The optimum transesterification conditions to obtain the 98% purity of fatty acid methyl esters (FAMEs) are as follows: 1 wt.% potassium hydroxide catalyst, 20wt.% acetone and 5:1 methanol to oil molar ratio, reaction temperature of 40^0C and reaction time of 30 minutes. The water content is 104 ppm, methanol content in the final product 95 ppm, and the concentration of acetone in the products 247 ppm.

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Keywords: biodiesel fuel; waste cooking oil; co-solvent method; transesterification; base catalysts.

1. Introduction

The world's energy supply has historically been dominated by fossil fuels. Today, fossil fuels accounts for 77% of global primary energy[1]. However, fossil fuels are claimed to have serious side-effects to ecosystem and human health due to its emissions of greenhouse gases (GHGs). Increasing concentration of GHGs causes the globe becoming warmer and thus leads to dramatic and unpredictable changes

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changes in climate. Therefore, finding alternative energies to replace fossil fuels is of vital importance for a sustainable future. Among alternative energies that have been known, biodiesel fuels (BDF) is proved to play a huge important role in the global movement away from fossil fuel.

Brazil has been leading in promoting biofuel since 1970s. Under the ProAlcool program, all gas stations in this country are required to sell ethanol-blended gasoline. In addition to Brazil, mandates for blending biofuel into vehicle fuels have appeared in several other countries in recent years, for example: The United States, China, India have been initiating their National Biodiesel Plans [2]. Following the global trend, Vietnam has acquired some achievements in producing BDF from domestic sources such as soybean, catfish and waste cooking oils.

BDF is a non-toxic, biodegradable, renewable fuel [3- 5] that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oilseed plants. BDFs produce fewer harmful emissions during production and combustion, and reduce carbon dioxide emissions to the atmosphere by 78%[6]. In addition, BDF is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability.

In general, BDF can be produced from either edible or non-edible oils[7-14]. However, researches have shown that producing BDF from edible sources pose a threat to global food security. The switch to researching the potential of non-edible BDF production feed stocks is now being taken into careful consideration for the purpose of continuing BDF production while not negatively affecting the food industry. In Hanoi, food processing manufactures, restaurants and hotels release approximately 30-40,000 tons of waste cooking oils per annum. A small portion is used to produce foods for animal, while the large remaining part is thrown away, which causes an environmental pollution. Therefore, the project for BDF production from waste cooking oil has practical significance.

Currently, biodiesel is mostly produced through transesterification between oil and methanol in the presence of alkaline KOH catalyst. Conventional methods of biodiesel production show disadvantages as implemented in a large scale. Some typical disadvantages: low level of triglycerides conversion, or difficulty in phase separation of the products, or high energy consumption, or high amount of waste which negatively affects the environment. Thus, there is a need to investigate new production methods which can overcome such disadvantages.

"Biodiesel" is the name given to an alternative diesel fuel that is produced from vegetable oils, recycled cooking greases, or animal fats. It consists of the simple alkyl esters of fatty acids, most typically the methyl esters[15]. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature versus conventional diesel, which is a fossil fuel leading to a potential exhaustion [11]. Vegetable oils, such as soybean oil, rapeseed oil (canola oil), and in countries with more tropical climates, tropical oils (palm oil and coconut oil) are the major sources of biodiesel. However, in recent years, animal fats and especially recycled greases and used vegetable oils have found increasing attention as sources of biodiesel, the latter primarily as inexpensive feed stocks [16].

In this research, the green co-solvent method was applied to produce biodiesel from waste cooking oil(WCO). This new method is more environmental-friendly and advantageous compared to the conventional alkali catalyzed transesterification method. Acetone was used as co-solvent in the alkali catalyz transesterification. The presence of acetone will increase the mutual solubility of methanol and waste cooking oil. This results in higher reaction yield, less soap formed, shorter time of reaction separation, and washing. However, the use of co-solvent method with acetone, the problem arises the removal of from mixture of products. In this study we survey study the optimum transesterification products such á to produce the hight quality BDF, the concentration of methanol, acetone and water content in the procurement process for high quality BDF.

Table 1 Chemical and physical properties of WCO used in this study

Properties	Unit	Average
Density	g cm^{-3}	0.901
Free fatty acid	wt.%	0.92
Water content	mg g^{-1}	1231.3
Oleic acid(C18:1)[a]	wt.%	53.8
Linoleic acid(C18:2)[a]	wt.%	23.5
Linolenic acid(C18:3)[a]	wt.%	11.8
Palmitic acid(C16:0)[a]	wt.%	5.7
Stearic acid(C18:0)[a]	wt.%	2.7
Other fatty acid	wt.%	2.5
Mean molecular weight of Free Fatty Acid in WCO	g mol^{-1}	281.6

2. Experimental

2.1. Material

Waste cooking oil was supplied by a local restaurant in Hanoi.
The physical and chemiacal properties of WCO are shown in table 1. KOH (grade 95.5 %), Methanol (grace 99%), Acetone (grade 99.7%), Acetonitrile (grade 99.7%), Isopropanol (grade 99%) were purchased from Wako Pure Chemical Industries, Osaka, Japan, and used without further purification. Chemical standards such as methyl oleate, methyl linoleate, diolein and triolein, were obtained from Sigma-Aldrich, Tokyo, Japan.

2.2. Proceduce

2.2.1. **The procedure of biodiesel production:** is carried out according to the flowing chart represented in Figure 1.

A twenty gram of waste cooking oil was mixed with a specified volume of acetone in a 250ml spherical flask. The flask was then put in a thermal reservoir on a heatable magnetic stirrer. Stir the mixture at 300-400rpm for about 2-3 minutes. Quickly pour a mixture of potassium hydroxide with methanol (prepared separately) into the flask.

After a specified period of time, stop the reaction and pour the mixture into a separatory funnel. Wait for the mixture to separate into 2 phases: crude fatty acid methyl ester (FAME) in the upper layer and glycerol in the lower layer. After removal of glycerol Crude BDF was neutralized with 5% H_3PO_4 solution once and several times with water afterward until obtaining a neutralized product, then dried by water distillation under reduced pressure.

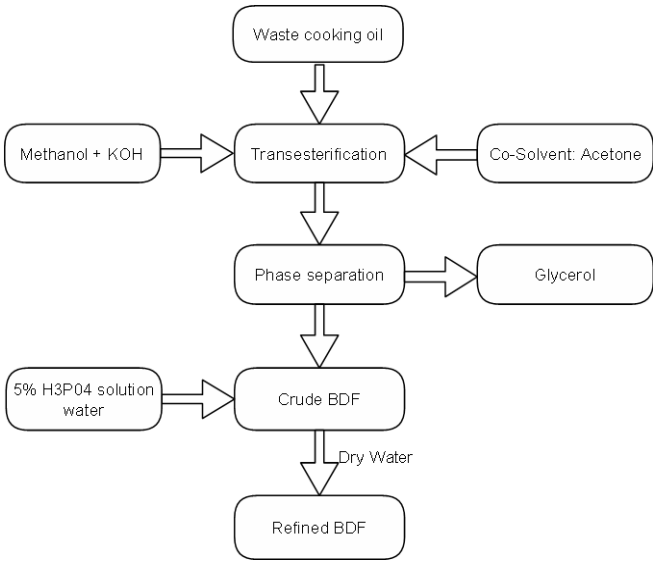


Fig. 1. The procedure of biodiesel production by co-solvent method

2.2.2. In process for analysis water content, methanol and acetone in BDF

We used a small device about 5 liters pilot plant to perform the reaction:

The reaction was carried out in the conditions as follow:

+ Waste cooking oil : 3 litter
+ The molar Methanol/WCO(mol/mol) = 6/1
+ Catalyst amount (KOH) = 1%(Wt.)
+ Solvent amount (Acetone) = 10%(Wt.)
+ Reaction temperature = 30^0C (room temperature)
+ Reaction time 60 minute

After the end of the reaction, the reaction mixture is split in two phases; The lower phase was a mixture of glycerine, acetone, methanol residues, water, and KOH, mix the ingredients mainly including FAME and acetone, residual methanol, KOH.

Phase separation time of about 2 hour. the phase separation process is finished, we removed the lower phase (phase glycerine) out of the mix. and conduct low-pressure distillation to remove acetone and methanol at 50^0C. remove the acetone and methanol approximately 1 hour, in this process we conducted sampling at different time: 5 min, 10 min, 20 min, 30min, 60 min. for analysis to determine the amount of water and acetone, methanol remaining. after almost complete removal of acetone and methanol we conduct FAME mixture washed with water to remove KOH.

water washing process is done 3 times and the volume of water is used per volume is 20% of FAME. after checking aqueous cleaning PH of 7, will end by water washing process. then we proceed to distill the water to obtain a mixture of pure FAME:

Dehydration is performed at different temperatures: 50,60,70,80^0C and in this process we conducted sampling at different time intervals to identify tick methanol concentration, acetone and water content remaining.

2.3. Analysis

2.3.1. Acid Value (AV) or FFA (Free Fatty Acid) Determination

Acid value (AV) is the mass of potassium hydroxide in milligrams that is required to neutralize 1 gram of vegetable oil or fat.

FFA constituent is Percentage of FFA (%FFA) in vegetable oil or fat.

Free fatty acid contained in raw materials has significant influence on alkali catalyzed transestrification process. If the free fatty acid constituent is higher than 3%, soap will appear during the BDF production process, which makes it difficult for washing and separating products. Hence, AV and %FFA need to be determined.

Procedure:

% FFA of waste cooking oil was determined by titration method. Weight 1g of waste cooking oil in a 50ml beaker. Pour 10ml of isopropanol into the beaker. Drop 3-4 drops of phenolphthalein indicator into the beaker. Titrate the mixture by 0.01N KOH solution.

%FFA is calculated according to following formula:

$$\%FFA = \frac{C_{KOH} \times V_{KOH} \times M_{free\ fatty\ acid}}{1000} \times 100$$

Where: C_{KOH} is molarity of KOH solution

V_{KOH} is volume of KOH solution

Percentage FFA can be coverted into AV by multiplying by 1.99

$$AV = \%\ FFA \times 1.99$$

The calculated % FFA of waste cooking oil was 1.0%, which means alkali-catalyzed transesterification can be used to produce biodiesel from waste cooking oil.

2.3.2 Determination of water content

Water content in raw materials and products as determined by Karl Fisher Moisture Titrator machine MKC-501(Tokyo electronic MFG.CO., LTD Japan)

2.3.3. Determination of reaction conversion

The concentrations of TG, DG, FAME, MG is determined by Gel Permeation Chromatography (GPC). The GPC apparatus consists of a pump (Shimadzu, LC 10AD). A column is (Asahipak GF 310 HQ, 300x7.5mm) and a refractive index detector (Shimadzu, RID-10A). The column oven was fixed at 30^0C, the mobile phase is acetone, the flow rate is 0.5ml.min^{-1} and the sample injection volume was 20 µL.

The FAME yields of the transesterification reaction is caclculated by the formula [7]:

$$FAMEYield(\%) = \frac{W_{FAME} / M_{FAME}}{3W_{WCO} / M_{WCO}} \times 100$$

W_{FAME} and W_{WCO} is the weight of FAME in FAME phase and the weight of WCO used.

M_{FAME} and M_{WCO} is the molecular weights of the FAME and the WCO .

2.3.4. Determination of Methanol and Acetone content in BDF

The concentrations of acetone and methanol in BDF are determined by GC-FID Agilent. Fused sillica capillary column 30m × 0.025mm ×0.2 µm film thickness was used. The temperature program for the gas chromatography was as follows. Initial temperature of 40°C was kept for 1 min, then the temperature was increased to 60°C at a rate of 2°C / min, final temperature is increased to 250°C with a speed 20°C/min. The infector temperature was 250^0C, and injection was performed in the splitless mode(1:50), the injection volume was 1µl. The carrier gas was air 450ml/min and hidrogen 40ml/min and helium 44ml/min make up gas.

3. Result and discussion

3.1. Production biodiesel from WCO

3.1.1. Influence of methanol/oil molar ratio on transesterification yield

Following the procedure described in figure 2, reactions were carried out with the conditions of 20g of waste cooking oil, 25 wt% of acetone, 1.5 wt% of KOH at 40°C in 1 hour.

Methanol/oil molar ratio was varied from 3:1 to 7:1. As can be seen in Figure 2, the transesterification yield increased as the methanol/oil molar ratio is below 5/1. When the molar ratio reached 5/1 and above, the yield attained 98% and remained constant afterward. Therefore, it can be concluded that the methanol/oil molar ratio of 5/1 is totally favorable for best yield of transesterification.

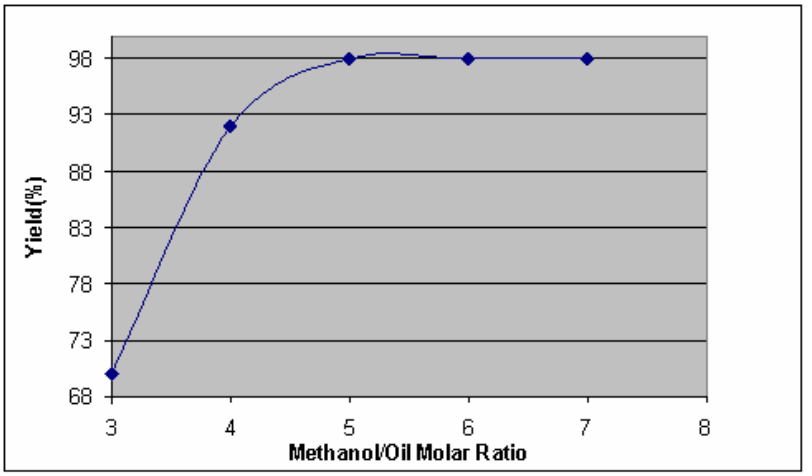


Fig. 2. Influence of methanol/oil molar ratio on transesterification yield

3.1.2. Influence of catalyst content on transesterification yield

Following the procedure described in Fig. 1, reactions were carried out with the conditions of 20g of waste cooking oil, methanol:oil molar ratio of 5:1, 25 wt% of acetone at 40^0C in 1 hour.

Catalyst amount was varied from 0.75 wt% to 2.0 wt% . As can be seen in Figure 3, the transesterification yield increased as the catalyst amount is below 1%. When the amount of KOH reached 1wt% and above, the yield attained 98% and remained constants afterward. Therefore, it can be concluded that the KOH amount of 1wt% is totally favorable for further study

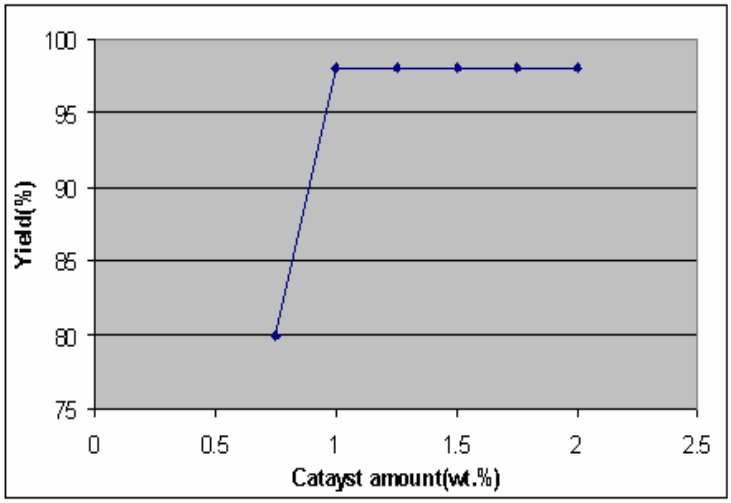


Fig.3. Influence of catalyst on transesterification yield

3.1.3. Influence of solvent on transesterification yield

Following the procedure described in Figure 1, reactions were carried out with the conditions of 20g of waste cooking oil, methanol : oil molar ratio of 5:1, 1 wt% of KOH at 40^0C in 1 hour.

Solvent amount was varied from 5 wt% to 40 wt% . As can be seen in Figure 4, the transesterification yield attained its highest value at 98% when the amount of acetone was 20%. The results showed that when increasing the solvent amount to 30 wt% and 40 wt%, the reaction yield considerably decreased. A explaination for this case is when the amount of acetone increased more than 20%, the concentration of reaction mixture decreased, which affected the reaction rate. In addition, acetone residual might have dissolved a part of FAME; the yield was reduced consequently.

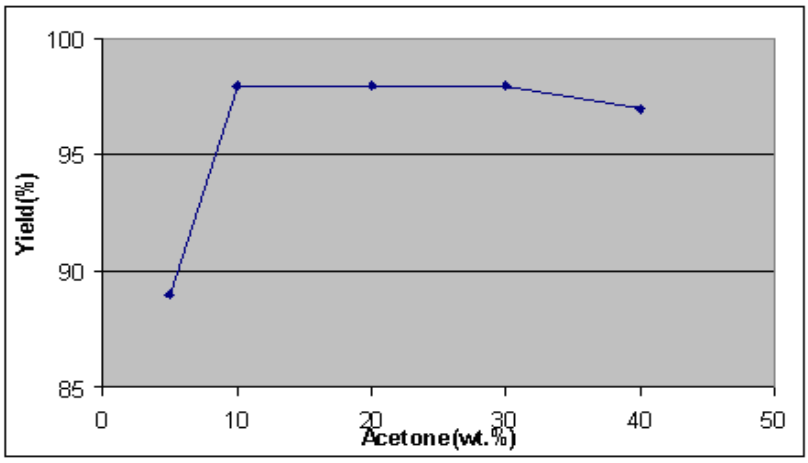


Fig.4. Influence of solvent on transesterification yield

3.1.4. Influence of Reaction Time on Transesterification Yield

Following the procedure described in Figure 1, reactions were carried out with the conditions of 20g of waste cooking oil, methanol/oil molar ratio of 5:1, 20 wt% of acetone, 1 wt% of KOH at 40^0C.

Reaction time was varied from 5 minutes to 60 minutes. As can be seen in Fig. 5, the transesterification yield increased as the reaction time below 23 minutes. The yield attained 98% when the reaction time is more than 23 minutes. Therefore, it can be concluded that the reaction time of approximately 23 minutes is totally favorable for further study.

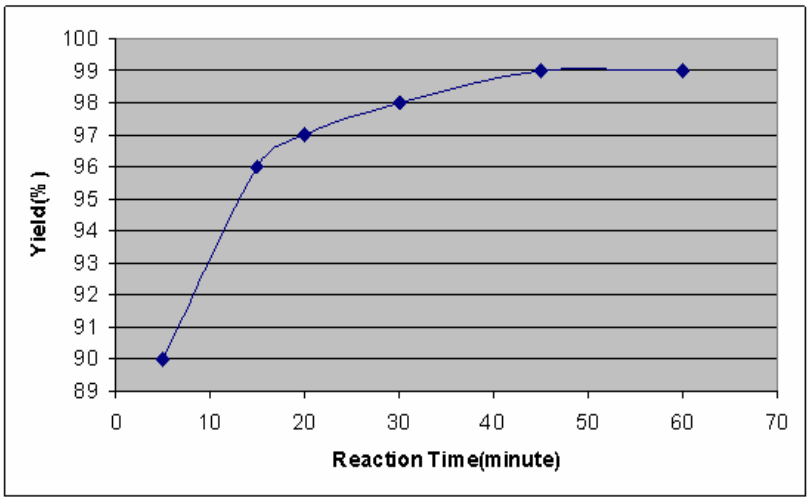


Fig. 5. Influence of reaction time on transesterification yield

3.1.5. Influence of temperature on transesterification yield

Following the procedure described in Fig.1, reactions were carried out with the conditions of 20g of waste cooking oil, methanol : oil molar ratio of 5:1, 20 wt% of acetone, 1wt% of KOH in 20 minutes.

Temperature was varied from 30^0C to 60^0C. As can be seen in Figure 6, the transesterification yield increased as the temperature below 40^0C. The yield attained 98% when the temperature is more than 40°C. Therefore, it can be concluded that the temperature of 40°C is totally favorable for further study.

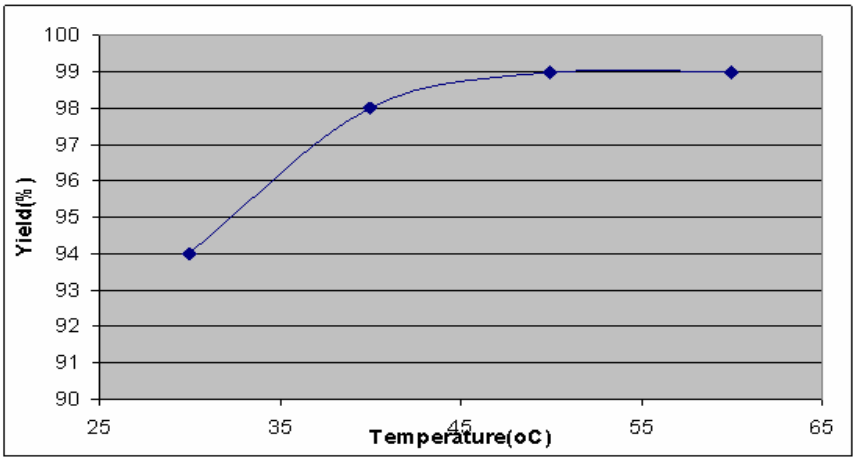


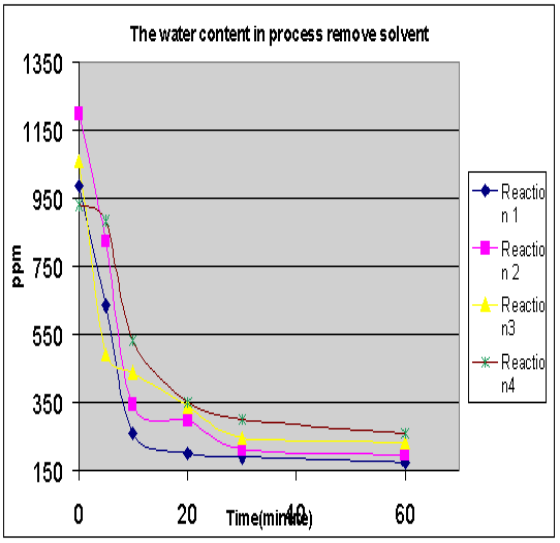
Fig.6. Influence of temperature on transesterification yield

3.2. Determine the amount of water, methanol and acetone in the refining process to obtain pure BDF

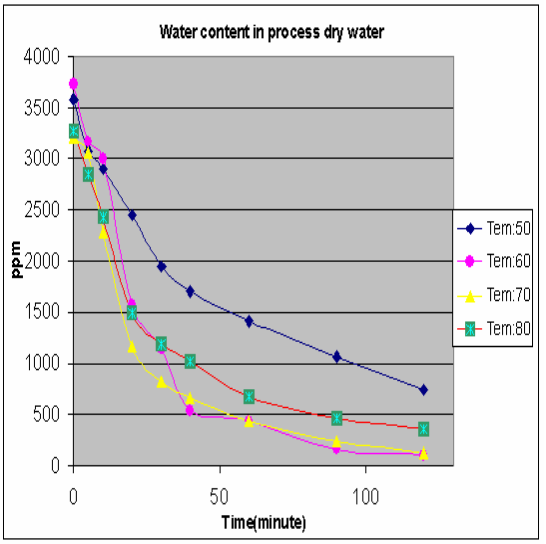
3.2.1. Water content

water content in biodiesel is not good for the engine and hard to preserve BDF after production, so we exploratory research to find appropriate conditions to reduce the water content in biodiesel at its lowest. The results are presented in Figure 7.

we can see from the Fig.7 , in the process of removing the solvent water content also decreased over time from 1000 ppm to 200 ppm, but in the process the product after solvent removal by water, and in the process dry drowning product to collect the final product, in BDF water content reduced from 3000 ppm to 200 ppm after about two hours.



(a)



(b)

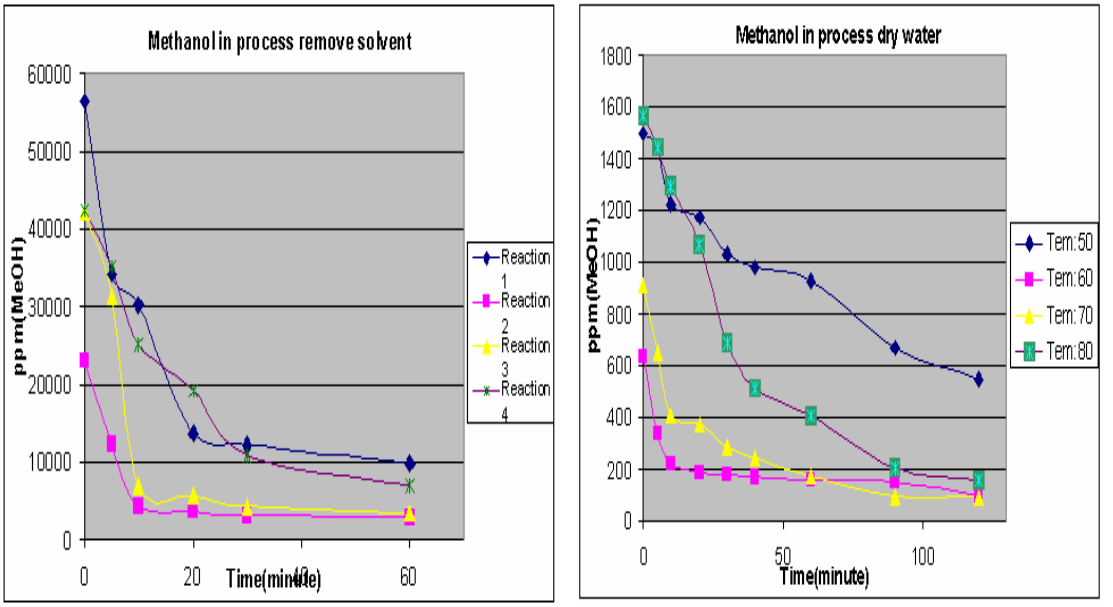
Fig.7. (a) Water content in process remove solvent

(b) Water content in process dry water

3.2.2. Methanol content

In reaction to form BDF is transesterification, methanol is used more often than the calculated amount, so to obtain the final product BDF, we purified to remove the product from methanol to give a concentration allowed. So we studied to find the best process for removing methanol from the product, the survey results are presented in Figure 8.

from the third graph we can see that the methanol content in descending BDF during solvent removal and water removal process.



(a) (b)

Fig. 8. (a) Methanol content in process of remove of solvent

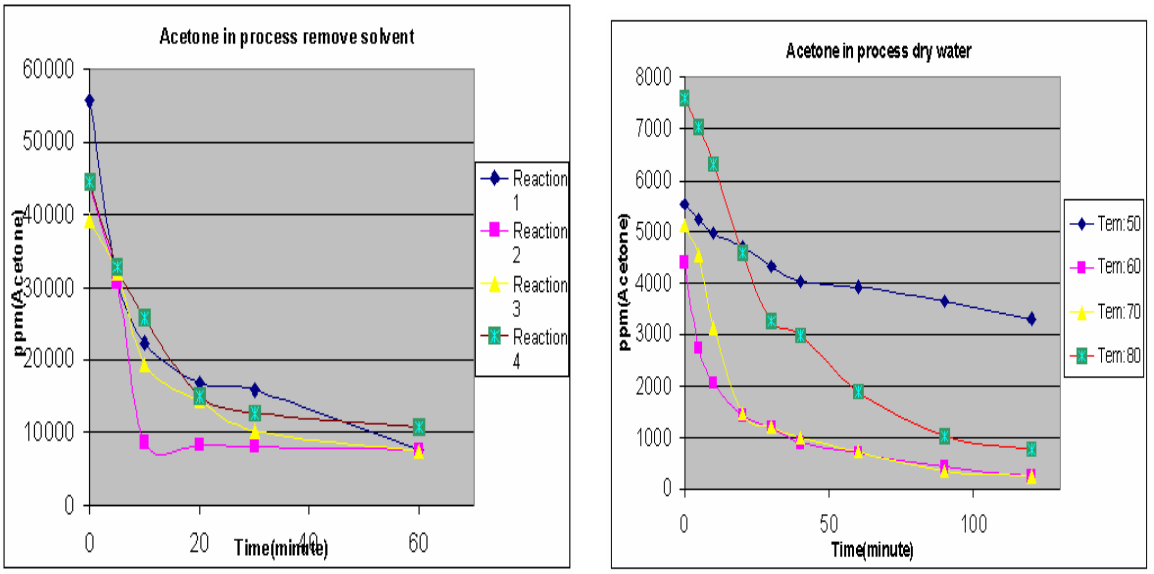
(b) Methanol content in process of dry water

From Figure 8 we can see, in both the process of removing methanol in BDF, in the process of removing the solvent methanol concentration decreased from 23039 ppm down as low as 2820 ppm. Then comes the drying process water methanol content in the final product obtained is 95 ppm in the temperature of 60^0C and 70^0C.

3.2.3. Acetone content

When co-solvent used in the preparation of biodiesel here we used acetone solvent. So after the reaction has a remaining amount of acetone in the BDF, in this study, our aim is to study the best conditions to remove the product from acetone and acetone concentrations allowed in the composition of of BDF. The results are presented in Fig.9. From Figure 9 we can see, in the process of removing the solvent acetone concentration decreased gradually and at the end of the remaining acetone concentrations

as low as 7392 ppm, then when the process of removing the water content of acetone 247 ppm is finally obtained at temperatures of 60^0C and 70^0C.



(a) (b)

Fig. 9. (a) Acetone content in process of remove of solvent

(b) Acetone content in process of dry water

4. Conclusion

By co-solvent method, the transesterification reaction needs the following conditions: reaction temperature: 40°C, molar MeOH / oil ratio: 5/1, KOH catalyst concentration: 1wt.%, acetone amount : 20wt.%, reaction time: 30 minute. BDF was obtained with 98% conversion.

we have the conditions that apply to survey water content, content of methanol and acetone concentrations in the production process at pilot scale BDF. The water content in the final product BDF is 104 ppm, methanol concentration was 95 ppm and acetone content is 247 ppm.

Acknowledgements

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